



Formation of
secondary aerosols
from gasoline vehicle
exhausts

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Formation of secondary aerosols from gasoline vehicle exhausts when mixing with SO₂

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Abstract

Sulfur dioxide (SO₂) can enhance the formation of secondary aerosols from biogenic volatile organic compounds (VOCs), but its influence on secondary aerosol formation from anthropogenic VOCs, particularly complex mixtures like vehicle exhausts, is still poorly understood. Here we directly co-introduced gasoline vehicles exhausts (GVE) and SO₂, a typical pollutant from coal burning, into a smog chamber to investigate the formation of secondary organic aerosols (SOA) and sulfate aerosols through photooxidation. In the presence of high concentration of SO₂, new particle formation was enhanced while substantial sulfate was formed through the oxidation of SO₂. The homogenous oxidation by OH radicals contributed a negligible fraction to the conversion of SO₂ to sulfate, and instead the oxidation by stabilized Criegee intermediates (sCIs), formed from alkenes in the exhaust reacting with ozone, dominated the conversion of SO₂. After 5 h of photochemical aging, GVE's SOA production factor revealed an increase by 60–200 % in the presence of high concentration of SO₂. This increase could largely be attributed to acid-catalyzed SOA formation, which was evidenced by the strong positive linear correlation ($R^2 = 0.97$) between the SOA production factor and in-situ particle acidity calculated by AIM-II model. A high-resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS) resolved OA's relatively lower oxygen-to-carbon (O : C) and higher hydrogen-to-carbon (H : C) molar ratios for the GVE/SO₂ mixture, with a much lower estimated average carbon oxidation state (OS_c) of -0.51 ± 0.06 than that of -0.19 ± 0.08 for GVE alone. The relative higher mass loading of OA in the experiments with SO₂ might be the major reason for the lower oxidation degree of SOA.

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1 Introduction

As main components of fine particles or PM_{2.5}, sulfate and organic aerosols (OA) can lead to serious and complex air pollution (Parrish and Zhu, 2009) and have negative effects on human health (Nel, 2005). Furthermore, sulfate and OA affect radiative forcing on global scale (Andreae et al., 2005; Shindell et al., 2009). A detailed understanding of the magnitude and formation pathways of sulfate and OA is therefore critical to formulate control strategies and accurately estimate their impact on air quality and climate, yet this attempt is often complicated due to the missing or underestimated oxidation pathways of sulfur dioxide (SO₂) (Berglen et al., 2004), which is the precursor of sulfate, and the unclear formation mechanisms of secondary organic aerosols (SOA) (de Gouw et al., 2005; Heald et al., 2005; Johnson et al., 2006; Volkamer et al., 2006), which account for a large fraction of OA (Zhang et al., 2007).

SO₂, mainly emitted from coal-fired power plants and coal-burning boilers, when mixed with gasoline vehicle exhausts containing a plenty of NO_x and aromatics that provide precursors for the formation of secondary nitrates and organic aerosols, might react with each other and make the formation of sulfate and SOA complicated. The alkenes present in gasoline vehicle exhausts can react with ozone to form stabilized Criegee intermediates (CIs), which were recently considered to significantly oxidize SO₂ and thus influence the formation of sulfate (Mauldin et al., 2012; Welz et al., 2012). On the other hand, recent smog chamber simulations indicated that SO₂ could enhance the SOA formation from typical biogenic precursors, such as monoterpenes and isoprene through acid-catalyzed reactions (Edney et al., 2005; Kleindienst et al., 2006; Jaoui et al., 2008), but the influence of acid-catalyzed reactions on SOA formation from aromatics is still debatable (Cao and Jang, 2007; Ng et al., 2007). In addition, these combinations of several pure chemicals could not well represent the mixing of SO₂ with vehicle exhausts brimming with thousands of gaseous and particle-phase components (Gordon et al., 2014) in the formation of secondary aerosols under real

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atmospheric conditions. Till present no reports are available about the influence of SO₂ on the formation of secondary aerosols from complex vehicle exhausts.

Here we directly introduced pipe exhausts from light-duty gasoline vehicles (LDGV) and SO₂ into a smog chamber with a 30 m³ Teflon reactor (Wang et al., 2014), to study the production of secondary aerosols: the influence of LDGV exhausts on the oxidation of SO₂ to form sulfate aerosols and reciprocally that of SO₂ on the formation of SOA from primary organics in LDGV exhausts.

2 Materials and methods

2.1 Vehicles and fuel

Three LDGVs were used in this study, one Euro 1 and two Euro 4 vehicles. They are all port fuel injected vehicles with model years ranging from 2002 to 2011. More details of the individual vehicles are listed in Table 1. All the vehicles were fueled with Grade 93# gasoline, which complies with the Euro III gasoline fuel standard. Details of the gasoline composition can be found elsewhere (Zhang et al., 2013).

2.2 Smog chamber experiments

Six photochemical experiments of LDGV exhaust were conducted in a 30 m³ indoor smog chamber in Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIG-CAS). The details of the smog chamber were described by Wang et al. (2014). Briefly, black lamps (1.2 m-long, 60 W Philips/10R BL, Royal Dutch Philips Electronics Ltd, the Netherlands) are used as light source, providing a NO₂ photolysis rate of 0.49 min⁻¹. Two Teflon-coated fans are installed inside the reactor to guarantee well mixing of the introduced gas species and particles within 120 s. In this study the temperature and relative humidity in the reactor were controlled at around 25 °C and 50 %, respectively. Before the introduction of vehicle exhaust, the vehicles were running on-

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Wu, 2008; Zhang et al., 2010, 2012, 2013) and a commercial proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS, Model 2000, Ionicon Analytik GmbH, Austria) (Lindinger et al., 1998; Jordan et al., 2009). C₂–C₃ and C₄–C₁₂ hydrocarbons were measured by GC-FID and GC-MSD, respectively. PTR-TOF-MS was used to determine the time-resolved concentrations of VOCs such as aromatics. The decay curve of toluene was used to derive the average hydroxyl radical (OH) concentration during each experiment.

Particle number concentrations and size distributions were measured with a scanning mobility particle sizer (SMPS, TSI Incorporated, USA, classifier model 3080, CPC model 3775). An aerosol density of 1.4 g cm⁻³ was assumed to convert the particle volume concentration into the mass concentration (Zhang et al., 2005). A high-resolution time-of-flight aerosol mass spectrometer (HR-TOF-MS, Aerodyne Research Incorporated, USA) was used to measure the particle chemical compositions and nonrefractory PM mass (Jayne et al., 2000; DeCarlo et al., 2006). The instrument was operated in the high sensitivity V-mode and high resolution W-mode alternatively every two minutes. The toolkit Squirrel 1.51H was used to obtain time series of various mass components (sulfate, nitrate, ammonium and organics). We used the toolkit Pika 1.1H to determine the average element ratios of organics, like H:C, O:C, and N:C (Aiken et al., 2007, 2008). The contribution of gas-phase CO₂ to the *m/z* 44 signal was corrected using the measured CO₂ concentrations. The HR-TOF-MS was calibrated using 300 nm monodisperse ammonium nitrate particles.

A summary of initial experimental conditions and final results is presented in Tables 2 and 3, respectively. Total wall-loss corrected OA varied from 17.8 to 91.4 μg m⁻³, which span the typical urban PM concentrations in those heavy polluted megacities with poor air quality. Primary OA (POA) concentrations of the experiments ranged from 0.13 to 0.31 μg m⁻³, which are negligible compared with the formed SOA. Initial mixing ratios of non-methane hydrocarbons (NMHCs) in the reactor were between 2.2 and 4.3 ppm, much higher than typical urban conditions. Though initial NMHCs, NO_x and average OH concentrations are different from typical urban conditions, we tried to maintain the

initial concentrations of the reactants as similar as possible for the same vehicle, so that all the changes in the SOA mass could be attributed to the effects of SO₂.

2.3 SOA production factors

SOA production factor (PF) (mg kg⁻¹) is calculated on a fuel basis:

$$PF = 10^6 \times [\text{SOA}] \times \left(\frac{[\Delta\text{CO}_2]}{MW_{\text{CO}_2}} + \frac{[\Delta\text{CO}]}{MW_{\text{CO}}} + \frac{[\Delta\text{HC}]}{MW_{\text{HC}}} \right)^{-1} \times \frac{\omega_{\text{C}}}{MW_{\text{C}}} \quad (1)$$

where $[\Delta\text{CO}_2]$, $[\Delta\text{CO}]$, and $[\Delta\text{HC}]$ are the background corrected concentrations of CO₂, CO and the total hydrocarbons in the reactor in $\mu\text{g m}^{-3}$; $[\text{SOA}]$ is the concentration of wall-loss corrected SOA in $\mu\text{g m}^{-3}$; MW_{CO_2} , MW_{CO} , MW_{HC} , and MW_{C} are the molecular weights of CO₂, CO, HC and C. ω_{C} (0.85) is the carbon intensity of the gasoline (Kirchstetter et al., 1999). The total hydrocarbons measured in this study include methane and C₂–C₁₂ hydrocarbons.

2.4 Determination of OH concentration

Decay of toluene measured by PTR-TOF-MS is used to determine the average OH concentration during each experiment. Changes in the toluene concentration over time can be expressed as:

$$\frac{d[\text{toluene}]}{dt} = -k \times [\text{OH}] \times [\text{toluene}] \quad (2)$$

where k is the rate constant for the reaction between toluene and OH radical. Assuming a constant OH concentration during an experiment, we can integrate Eq. (2) to get Eq. (3):

$$\ln \left(\frac{[\text{toluene}]_0}{[\text{toluene}]_t} \right) = k \times [\text{OH}] \times t \quad (3)$$

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So by plotting $\ln([\text{toluene}]_0/[\text{toluene}]_t)$ vs. time t , we can obtain a slope that equals $k \times [\text{OH}]$. The average OH concentration is therefore calculated as:

$$[\text{OH}] = \frac{\text{slope}}{k} \quad (4)$$

2.5 Determination of the steady state concentration of stabilized CIs

5 The production of stabilized CIs in the atmosphere is dominated by ozonolysis of alkenes (Heard et al., 2004).



The four main losses of CIs are reactions with H_2O , SO_2 and NO_2 and unimolecular decomposition.



The steady state concentration of CIs will be

$$15 \quad \text{CIs}_{\text{steady-state}} = \frac{\phi K_{\text{R1}}[\text{O}_3][\text{alkene}]}{K_{\text{R2}}[\text{H}_2\text{O}] + K_{\text{R3}}[\text{SO}_2] + K_{\text{R4}}[\text{NO}_2] + K_{\text{R5}}} \quad (5)$$

In this study, we estimated the steady state concentration of stabilized CIs throughout the whole experiment. The production rate of stabilized CIs depended on both the concentrations and composition of alkenes in the exhausts. Detailed gas-phase mechanisms of alkenes from the Master Chemical Mechanism version 3.3 or MCM v3.3 (http://www.chem.leeds.ac.uk/MCM) were run to determine the time-resolved concentrations of stabilized CIs in the experiments. Only the gas-phase mechanisms of

massive aerosols and gaseous species. He et al. (2014) found that SO_2 could react with NO_2 on the surface of mineral dust to promote the conversion of SO_2 to sulfate. In this study, the reaction between SO_2 and NO_2 on the surface of existed aerosols might be a pathway to lead to the formation of sulfate.

3.2 SOA production

Fuel-based SOA production factors (PF), expressed as SOA production in milligram (mg) after 5 h photooxidation of LDGV exhausts emitted when per kilogram (kg) gasoline was burned, all increased substantially when adding SO_2 , 60–200 % above that without SO_2 (Fig. 7a), although the selected cars' emission standards varied from Euro-I to Euro-IV. Accordingly when adding SO_2 , the in-situ particle acidities at the time when SOA formation rate peaks, calculated as H^+ concentrations based on AIM-II model $\text{H}^+ - \text{NH}_4^+ - \text{SO}_4^{2-} - \text{NO}_3 - \text{H}_2\text{O}$ with gas-aerosol partitioning disabled (<http://www.aim.env.uea.ac.uk/aim/model2/model2a.php>) (Clegg et al., 1998; Wexler and Clegg, 2002), were 1.6–3.7 times as high as those without adding SO_2 (Table 3). This elevated particle acidity could largely explain the higher PFs of SOA from LDGV exhausts with SO_2 , supported by the strong positive linear correlations ($R^2 = 0.965$, $P < 0.01$) between SOA PFs and the in-situ particle acidities (Fig. 7b). Aromatic hydrocarbons are important SOA precursors in gasoline vehicle exhausts (Nordin et al., 2013; Gordon et al., 2014; Liu et al., 2015). The influence of particle acidity on SOA formation from aromatics is still debatable. Cao and Jang (2007) found that the presence of acid seeds with $[\text{H}^+]$ concentrations of 240–860 nmol m^{-3} greatly increased the SOA yields from oxidation of toluene and 1,3,5-trimethylbenzene as compared with those using neutral seed aerosols. However, Ng et al. (2007) observed no influence of particle acidity on SOA yields from the aromatics, which might be due to the low content of aerosol water. In this study, SOA production from gasoline vehicle exhaust was enhanced even at a low level of $[\text{H}^+]$ concentrations ranging from 7.4 to 27.1 nmol m^{-3} . Gas-phase oxidation products of aromatic hydrocarbons in the exhausts, like multifunctional carbonyl glyoxal, would be transformed more quickly to low

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formed from LDGV exhausts with SO_2 when compared to that of -0.19 ± 0.08 without SO_2 , though they were all within or near the OS_c range of -0.5 – 0 for semi-volatile OOA (SV-OOA) (Aiken et al., 2008). The relatively lower OS_c with SO_2 indicated a lower oxidation degree of SOA. As Loza et al. (2012) did not observed a difference in H : C and O : C for m-xylene SOA with neutral and acidic seed particles, acid-catalyzed heterogeneous reactions might not influence the oxidation degree of SOA in this study. Shilling et al. (2009) observed a lower O : C of SOA formed from the dark ozonolysis of α -pinene at a higher mass loading of organic aerosols and suggested that the compounds partitioning into the particle phase at lower loadings were more oxygenated. Kang et al. (2011) also observed that the oxidation degree of OA decreased rapidly as the OA mass concentration increased for the same amount of OH exposure. Given that the average OH concentrations were similar for the same vehicle (Table 2), the relative higher mass loading of OA in the experiments with SO_2 might lead to the lower O : C and thus decrease the oxidation degree of OA.

4 Conclusion

We reported a series of chamber experiments investigating the formation of secondary aerosols from the mixture of SO_2 and gasoline vehicle exhaust. The high content of alkenes in gasoline vehicle exhaust formed a plenty of stabilized CIs, which dominated the formation of sulfate. On the other hand, the elevated particle acidity due to the formation of sulfuric acid enhanced the SOA production from gasoline vehicle exhaust. We concluded that SO_2 and gasoline vehicle exhausts can enhance each other in forming secondary aerosols. Consequently, high concentration of SO_2 and high levels of aerosol acidity together with rapid increase of LDGVs in heavy polluted cities such as Beijing (Pathak et al., 2009; He et al., 2014) would make the air quality worse if there were no stricter control strategies on emissions of SO_2 and vehicle exhausts. Previous studies indicated that the high content of alkenes in China's gasoline oil was not a good thing for the control of ozone in ambient air (Y. Zhang et al., 2013, 2015).

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Our results suggested that the incomplete combustion of gasoline with high content of alkenes might also induce the formation of stabilized CIs, which would facilitate the production of secondary aerosols. In China the limit of alkenes content was lowered to 24 % by volume in the newly established Level V gasoline fuel standard from 28 % by volume in the Level IV gasoline fuel standard. This limit is still quite higher when compared to those in USA or in Europe, and in particular, 6 times that in California, USA. Thus, limiting the content of alkenes in China's gasoline would benefit the control of both ozone and secondary aerosols.

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[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)**Table 1.** Detailed information of the three LDGVs.

ID	Emission standard class	Vehicle	Model year	Mileage (km)	Displacement (cm ³)	Power (kW)	Weight (kg)
I	Euro4	Golf	2011	25000	1598	77	1295
II	Euro4	Sunny	2011	9448	1498	82	1069
III	Euro1	Accord	2002	237984	2298	110	1423

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Table 2. Summary of the initial conditions during the photooxidation of LDGV exhausts.

Exp #*	OH ($\times 10^6$ molecules cm^{-3})	T ($^{\circ}\text{C}$)	RH (%)	VOC / NO_x	NMHCs (ppbv)	NO (ppbv)	NO_2 (ppbv)	SO_2 (ppbv)
I-1	0.88	25.0 ± 0.8	52.9 ± 2.0	9.3	2896	300.6	9.5	8.6
I-2	1.19	25.5 ± 0.3	53.6 ± 2.5	7.7	2323	281.4	19.5	151.8
II-1	1.29	24.6 ± 0.5	52.5 ± 1.7	10.8	4313	374	24.7	9
II-2	1.08	24.2 ± 0.7	55.9 ± 2.5	9	3220	356	2.6	151.9
III-1	0.73	24.1 ± 0.6	57.0 ± 2.0	6	2582	431	0.6	9.2
III-2	0.79	24.3 ± 0.3	57.9 ± 1.2	4.9	2243	454.6	3.9	154.1

* Photooxidation experiments of LDGV exhausts named with I, II and III refers to different vehicles.

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Table 3. Summary of the final results during the photooxidation of LDGV exhausts.

Exp #	POA ($\mu\text{g m}^{-3}$)	SOA ($\mu\text{g m}^{-3}$)	Sulfate ($\mu\text{g m}^{-3}$)	Ammonium ($\mu\text{g m}^{-3}$)	Nitrate ($\mu\text{g m}^{-3}$)	Particle number (cm^{-3}) ^a	[H ⁺] ^b (nmol m^{-3})
I-1	0.31	77.6	0.7	17.1	65.9	85182	12.5
I-2	0.21	91.2	67.5	17.6	6.1	563705	21.9
II-1	0.28	30.7	–	2.6	5.6	7427	10.4
II-2	0.13	37.3	38.1	9.7	1.9	357673	16.5
III-1	0.17	17.6	–	0.1	0.7	116143	7.4
III-2	0.23	77	76.7	19.2	5.3	630620	27.1

^a Maximum particle number concentrations were without wall loss corrections.

^b The concentration of H⁺ in particle phase shown here was the value when the SOA formation rate reached the maximum during each experiment.

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Table 4. Summary of the final results during the photooxidation of LDGV exhausts.

Stabilized Cls	$10^{15} K_{R2}$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	$10^{11} K_{R3}$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	$10^{12} K_{R4}$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	K_{R5} (s^{-1})
CH ₂ OO	0.025 ^a	3.9 ^b	7.0 ^b	0 ^c
CH ₃ CHOO	7.0 ^d	4.55 ^d	2.0 ^d	67.5 ^e
(CH ₃) ₂ COO	2.1 ^c	2.4 ^c	2.0 ^c	151 ^c

^a Ouyang et al. (2013); ^b Welz et al. (2012); ^c Newland et al. (2015); ^d Taatjes et al. (2013); ^e Average of K_{R5} from Fenske et al. (2000) and Newland et al. (2015).

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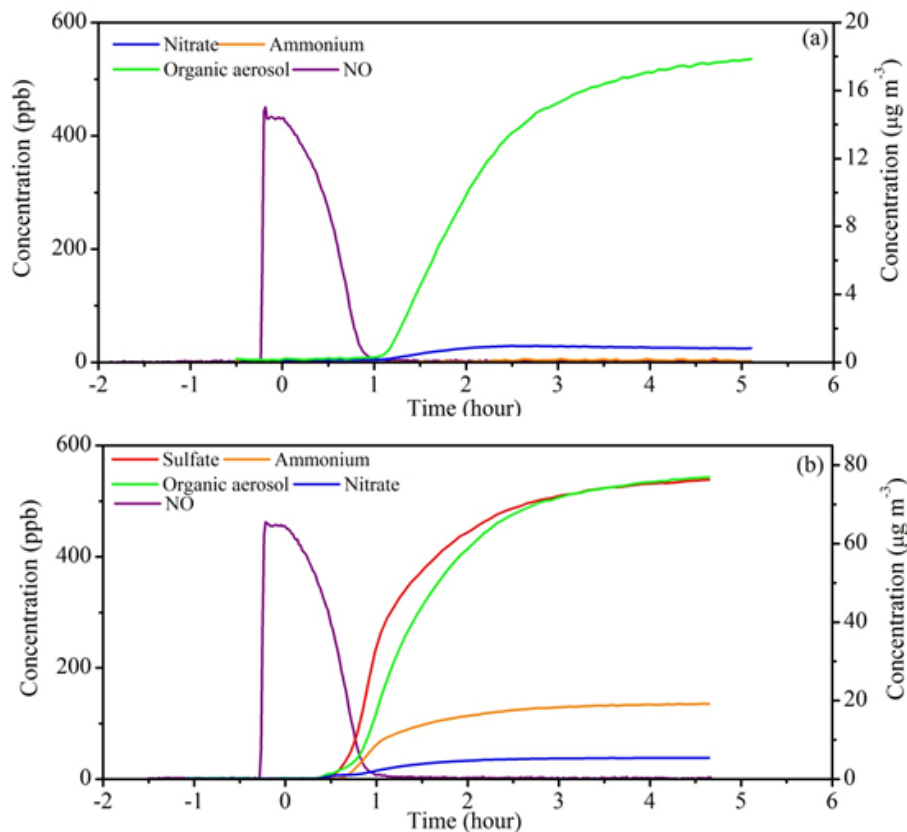


Figure 1. Concentration–time plots of NO (left y axis) and particle–phase species (right y axis) during the photochemical aging of emissions from vehicle III. **(a)** Without SO_2 , and **(b)** with SO_2 . At time = 0 h, the black lamps were turned on.

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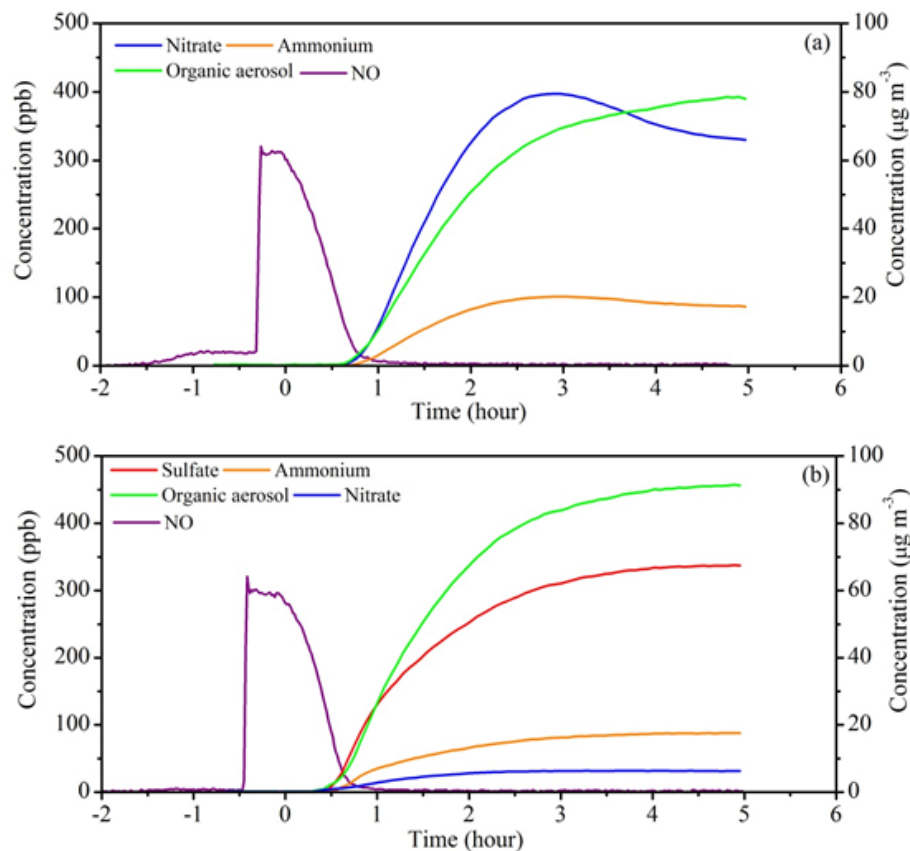


Figure 2. Concentration–time plots of NO (left y axis) and particle–phase species (right y axis) during the photochemical aging of emissions from vehicle I. **(a)** Without SO_2 , and **(b)** with SO_2 . At time = 0 h, the black lamps were turned on.

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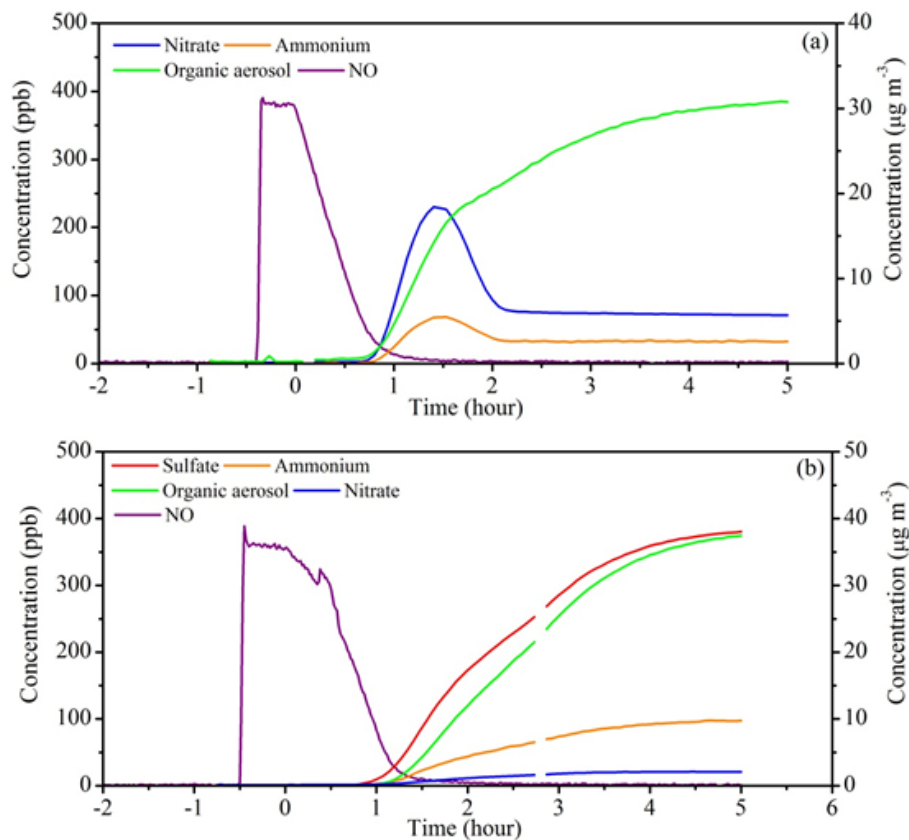


Figure 3. Concentration–time plots of NO (left y axis) and particle–phase species (right y axis) during the photochemical aging of emissions from vehicle II. **(a)** Without SO_2 , and **(b)** with SO_2 . At time = 0 h, the black lamps were turned on.

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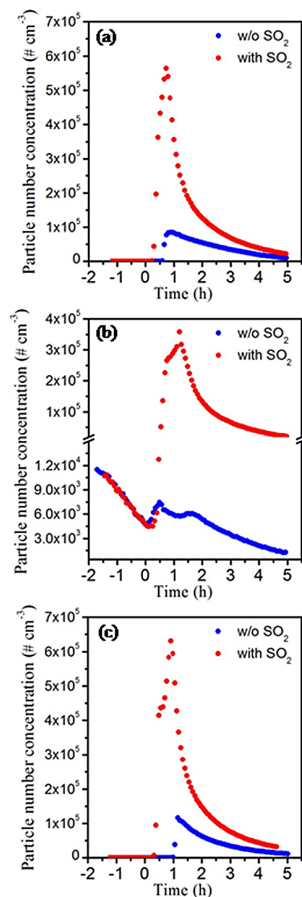


Figure 4. Evolution of particle number concentrations during the aging experiments of LDGV exhaust for vehicle I (a), II (b) and III (c). At time = 0 h, the black lamps were turned on. W/o SO₂ and with SO₂ in the figures represent experiments without and with adding SO₂, respectively.

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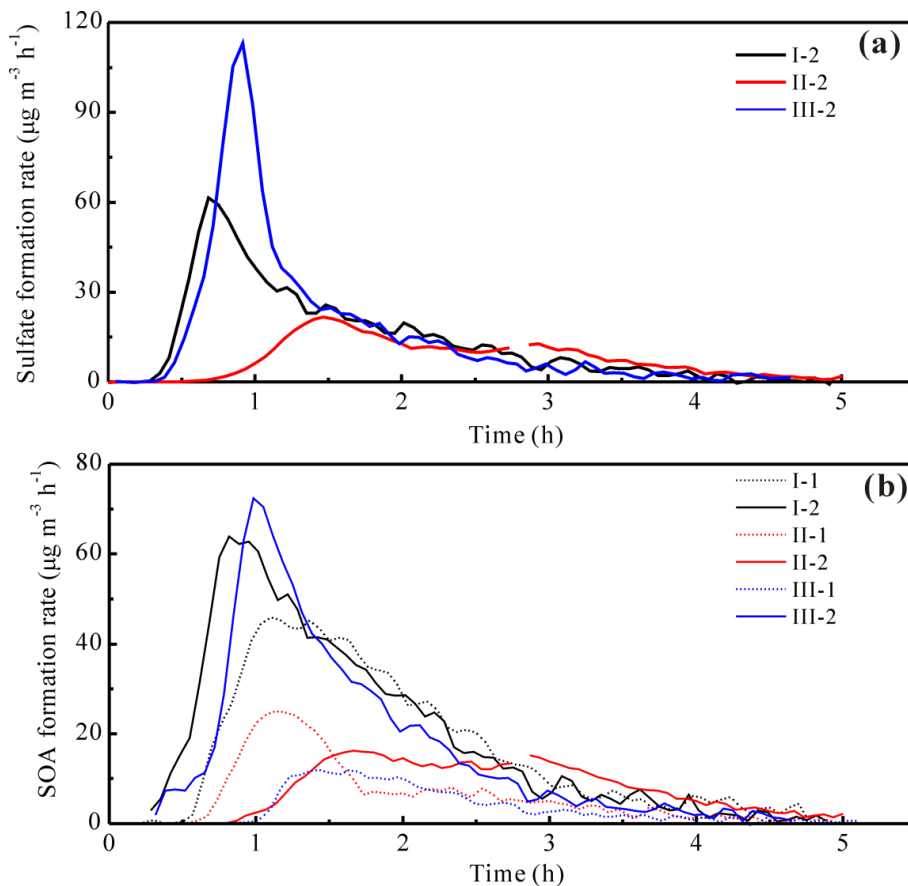


Figure 5. Sulfate formation rates (a) and SOA formation rates (b) as a function of time during the photooxidation of LDGV exhausts.

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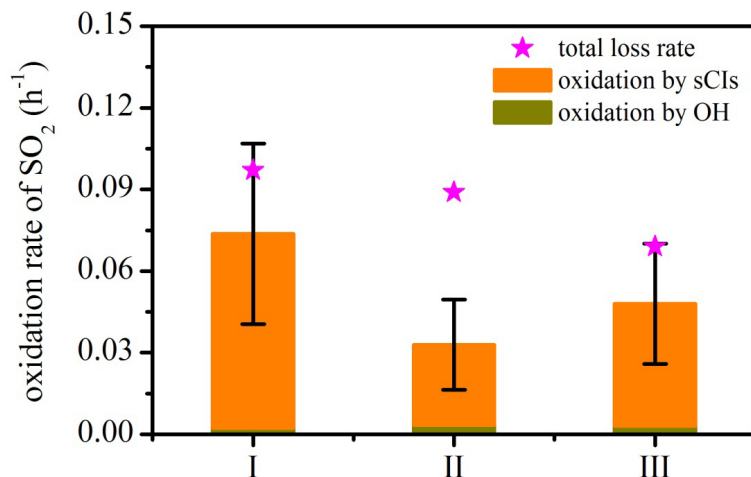


Figure 6. The oxidation rate of SO_2 during the photooxidation of LDGV exhausts with SO_2 . The loss rates of SO_2 reacting with OH radicals and stabilized CIs were calculated by multiplying the reaction rate coefficients derived from the MCM v3.3 by the average OH concentration and estimated stabilized CIs concentration, respectively. Error bars represent the standard derivation (1σ) of the oxidation rate of SO_2 by stabilized CIs throughout the whole experiment.

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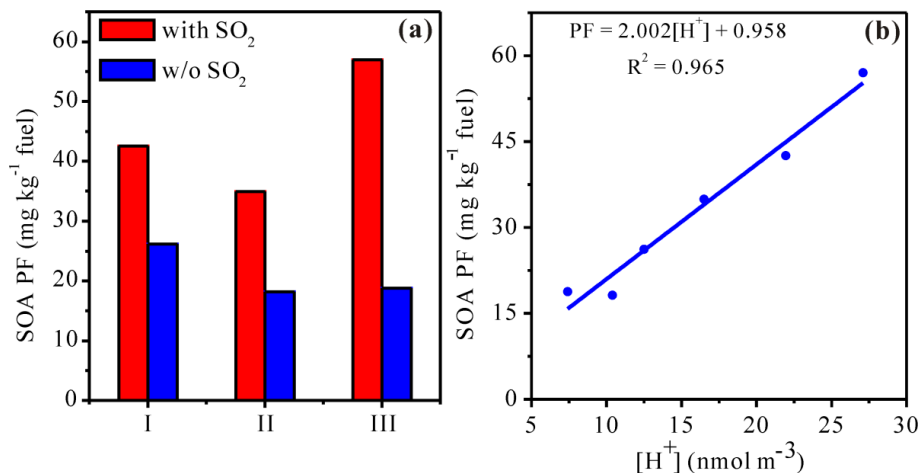


Figure 7. SOA production factor (PF) and its relationship with particle acidity. **(a)** SOA PF after 5 h of photochemical aging of exhausts from different LDGVs with and without additional SO₂. **(b)** SOA PF as a function of in-situ particle acidity. The concentration of H⁺ in particle phase shown here was the value when the SOA formation rate reached the maximum during each experiment.

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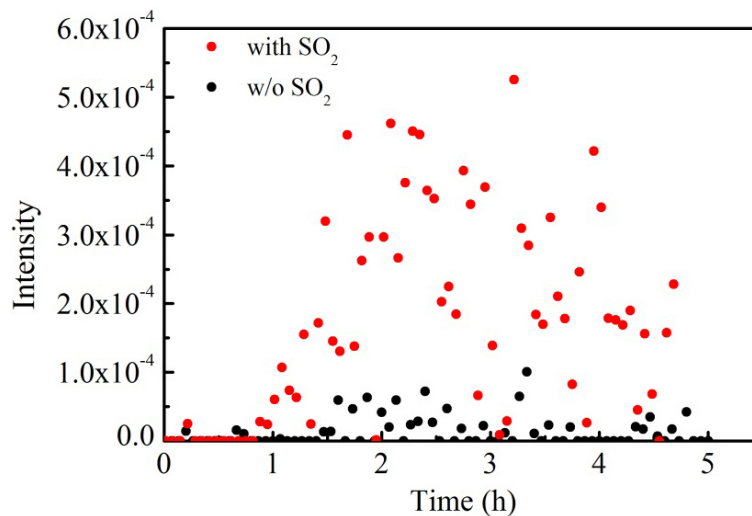


Figure 8. Time evolution of m/z 88 during the aging of LDGV exhaust from vehicle III.

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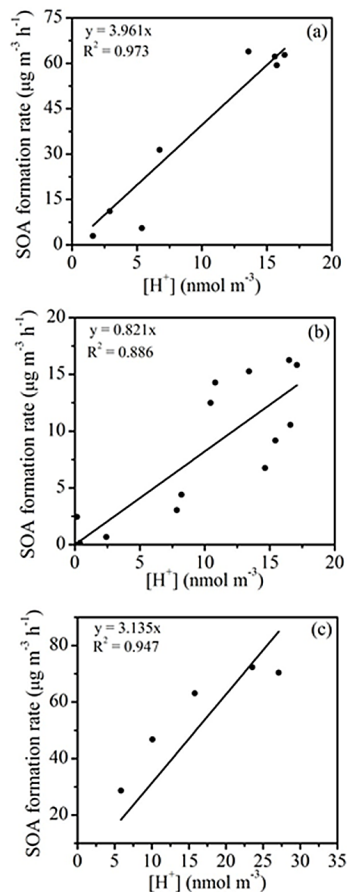


Figure 9. SOA formation rate as a function of in-situ particle acidity ($[\text{H}^+]$) for vehicle I **(a)**, vehicle II **(b)** and vehicle III **(c)** with adding SO_2 . Plotted data were selected from when SOA formation rate was higher than zero to when the rate reached the maximum value.

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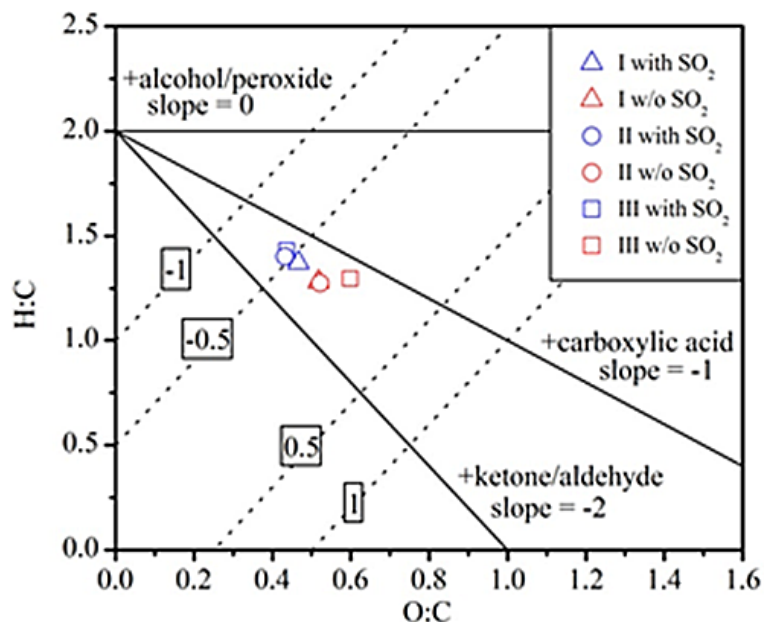


Figure 10. O : C vs. H : C of SOA formed from LDGV exhaust with and without additional SO₂ at the end of each experiment. Blue and red symbols represent data with and without additional SO₂, respectively. The dashed lines represent estimated average carbon oxidation states of -1, -0.5, 0.5 and 1 (Kroll et al., 2011). The black lines represent the addition of functional groups to an aliphatic carbon (Heald et al., 2010).

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